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ABSTRACT

The temperature dependence of the dielectric constant and dissipation factor of potassium alum crystals cut in the (111) planes has been determined over the temperature range 250°K to 300°K . Also, the temperature dependence of the dielectric constant and dissipation factor of powdered potassium alum and of powdered hydrated aluminum sulphate has been measured over the range 100°K to 300°K . The rapid increase in dielectric constant and dissipation factor of the powdered samples over the range 240°K to 300°K is attributed to the presence of adsorbed water.

thesis
1955(F)
#8

THE UNIVERSITY OF ALBERTA

"DIELECTRIC BEHAVIOUR OF POTASSIUM ALUM"

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY OF ARTS AND SCIENCE

DEPARTMENT OF PHYSICS

by

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EDMONTON, ALBERTA,

September 1955.

ACKNOWLEDGMENTS

The author wishes to thank Dr. H. Grayson-Smith for suggesting the problem which led to this thesis and for his guidance throughout the completion of the work.

He wishes to thank members of the Physics Department and Geology Department for their assistance. Also, he wishes to thank the National Research Council for a grant, enabling the work to be carried out during the summer months.

CONTENTS

<u>Chapter</u>	<u>Page</u>
I Introduction	1
II Theory	4
III Apparatus and Procedure	14
IV Discussion	30
Bibliography	34

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Bridge Circuit	12
2 Diagram of Condensers	22
3 Diagram of Assembled Apparatus	23
4 ϵ_0 and D vs. T for $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ crystals	24
5 ϵ and D vs. T for powdered $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 17H_2O$	25
6 $\epsilon, \bar{\epsilon}$ and D vs. T for powdered $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	26
7 ϵ and D vs. T for powdered $Al_2(SO_4)_3 \cdot 15H_2O$	27
8 ϵ and D vs. T for powdered $Al_2(SO_4)_3 \cdot 16H_2O$	28
9 α_0 vs. T for $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ crystals	29

I INTRODUCTION

Second order phase transitions in hydrates of chromium sulphate, chromium nitrate, nickel nitrate and cobalt nitrate were discovered by Vasileff and Grayson-Smith¹ by means of specific heat measurements on powdered samples of these salts. The transition temperatures were found to be 195° K, 158° K, 149° K, and 153° K respectively. Since investigation by Johnson and Grayson-Smith² had shown no magnetic irregularities at the transition temperatures, the dielectric properties of the salts were studied. Grayson-Smith and Sturrock³ found by measuring the variation of dielectric constant of the powdered salts that only hydrated chromium sulphate showed irregular behaviour at the transition temperature. Using results from the Vasileff and Grayson-Smith investigation together with his own data, Sturrock was able to show that the transition in chromium sulphate hydrate is consistent with that expected if two water molecules per molecule of salt are set free to orient themselves in the electric field. However, measurements on crystal plates of salt would be necessary in order to get accurate values of

¹Vasileff and Grayson-Smith, Can. J. Res. A 28, 367, 1950.

²Johnson and Grayson-Smith, Can. J. Res. A 28, 229, 1950.

³Grayson-Smith and Sturrock, Can. J. Phys. 30, 26, 1952.

the dielectric constant.

The growing of large chromium sulphate crystals was attempted by Young⁴ without success so the author carried out dielectric measurements on powdered samples of hydrated salts of which large crystals can be readily grown. If an irregularity in dielectric behaviour, like that in the hydrated chromium sulphate should be found, large crystals could be grown and measurements made on slices taken from these crystals.

Dielectric measurements on powdered aluminum sulphate were made both by Young and by the author without showing any dielectric anomalies. However, preliminary measurements with powdered potassium alum showed a small anomaly which might be significant. Since this material is easily crystallized, further work was concentrated upon it.

Besides the possible anomalies due to second order transitions, all the hydrated salts in powder form had shown a large increase of dielectric constant between 240°K and 300°K, accompanied by an apparent A.C. conductivity. Another purpose of the present research was to make a more complete study of this phenomenon, using crystal slices.

While the author has found no new data on second order transitions in hydrated salts because the small anomaly in

⁴Young, D.M., Some Dielectric Properties of Hydrated Chromic Sulfate, unpublished thesis, University of Alberta, 1953.

the dielectric constant of powdered potassium alum did not appear with large crystals, this investigation has furnished some information on the rapid rise of dielectric constant over the temperature range 240°K to 300°K .

II THEORY

Dielectrics are substances that are unable to conduct electric current, or present a very low conductivity to the passage of current. They may exist in any phase. Included in this class of substances are water, either solid, liquid or gaseous, acids such as hydrochloric in the solid form, salts such as sodium chloride and ammonium chloride in solid form and nitrogen or oxygen in solid, liquid or gaseous phases.

The dielectric constant is defined for isotropic substances as

$$\epsilon = 1 + 4\pi \frac{P}{E}$$

where E is the electrostatic field strength, assumed homogeneous, and P is the polarization, or the dipole moment per unit volume of the substance due to the presence of E .

The existence of P is due to the polarizability of the molecules of the specimen.

In general, there are three types of polarizabilities - electronic, ionic and orientational. Electronic polarizability is due to the displacement of the electron cloud surrounding each nucleus with respect to the nucleus, because of an external electric field acting on the atom.

Ionic polarizability arises from the displacement of

an ion with respect to other ions and also to the deformation of the electronic shell of the ion as a result of the relative motion of the ions.

Orientational polarizability is due to the orienting of molecules which possess a permanent dipole moment by the application of an external field.

An important theorem due to Fröhlich⁵ is that electronic and ionic polarizabilities, neglecting the presence of lattice expansion, are temperature independent since they arise from elastic displacement of charge, while orientational polarizability, which depends on the presence of permanent dipoles, is temperature dependent.

The dipole moment of a molecule resulting from its electronic and ionic polarizabilities is given by

$$\underline{m} = \underline{m}_e + \underline{m}_i \quad (1)$$

where \underline{m}_e , \underline{m}_i are its dipole moments due to electronic and ionic polarizability.

If the local electric field applied to the molecule is \underline{f} then

$$\underline{m}_e = \alpha_e \underline{f} \quad (2)$$

$$\underline{m}_i = \alpha_i \underline{f} \quad (3)$$

$$\underline{m} = (\alpha_e + \alpha_i) \underline{f} = \alpha_o \underline{f} \quad (4)$$

α_e is the electronic polarizability

⁵Fröhlich, H., Theory of Dielectrics, Oxford, 1950.

α_i is the atomic polarizability

α_o is the deformation polarizability

The local field \underline{f} can be calculated using the following assumptions:

(1) The local field is a sum of the external field plus the field due to the charge distribution on a spherical cavity cut out of the specimen with centre at the point where \underline{f} is being calculated;

(2) The field at the centre of the spherical cavity due to its interior charges is zero.

Using these assumptions \underline{f} is given by:

$$\underline{f} = \underline{E} + \frac{4\pi}{3} \underline{P} \quad \text{which is the Lorentz field. (5)}$$

The polarization \underline{P} is given by

$$\underline{P} = N \alpha_o \underline{f} \quad (6)$$

α_o is the deformation polarizability of the molecule

N is the number of molecules per unit volume.

If \underline{f} is assumed to be a Lorentz field,

$$\underline{P} = \left(\underline{E} + \frac{4\pi}{3} \underline{P} \right) N \alpha_o. \quad (7)$$

Since $\epsilon - 1 = 4\pi \frac{\underline{P}}{\underline{E}}$ by the definition of ϵ

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N \alpha_o. \quad (8)$$

This is the Clausius - Mosotti equation.

Orientational polarizabilities were first introduced by Debye in order to explain the large dielectric constant of water and alcohol. He assumed that certain molecules possessed a dipole moment even in the absence of an applied

field. Such moments are called permanent dipole moments. Using a statistical mechanical argument⁶ it is possible to relate the dipolar polarizability of a molecule to its dipole moment μ . The total molecular polarizability is then given by

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT} \quad (9)$$

Here α_0 is the deformation polarizability

k is the Boltzmann constant

T is the absolute temperature

This is the Langevin - Debye equation.

The Clausius - Mosotti equation is fairly reliable for non-polar substances but it completely fails in the case of polar substances. To see this failure, we substitute α of equation (9) into the Clausius - Mosotti equation, equation (8), neglecting α_0 .

We get
$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi N\mu^2}{3kT}$$

and
$$\epsilon = 1 + \frac{4\pi N\mu^2}{3k(T-T_c)} \quad (10)$$

where
$$T_c = \frac{4\pi N\mu^2}{9k}$$

For water, T_c has a value of about 1200°K , where spontaneous polarization should set in and the water become

⁶Kittel, C., Introduction to Solid State Physics - Wiley, New York, 1953.

ferroelectric. Such ferroelectric behaviour is not, however, observed in water.

This failure of the theory resulted in the rejection of the Lorentz value of the local field in the case of polar media. This was first pointed out by Onsager⁷, who showed that the use of the Lorentz expression for the local field assumes that the dipole moments of all the molecules are parallel. This assumption, however, does not hold for permanent dipoles which are more or less randomly oriented. Onsager carried out an approximate treatment for the case of polar media by considering a small spherical cavity just large enough to contain one molecule. He considered the polarization to be due to permanent dipoles only and neglecting all interaction except long range dipole interaction obtained the result

$$\frac{(\epsilon-1)(2\epsilon+1)}{\epsilon} = 12\pi N \left[\alpha_0 + \frac{\mu^2}{3kT} \right] \quad (11)$$

where μ is the permanent dipole moment of a molecule

N is the number of molecules per unit volume.

This relation is possibly the best arrived at yet for finding the variation of ϵ with T of a polar substance. But it is only an approximation, since the short range dipole interactions are neglected.

Either of eqns. (9) or (11) predicts that ϵ should

⁷ L.O. Onsager, J. Am. Chem. Soc. 58, 1486, (1936).

decrease with T when there are dipoles present. This behaviour can therefore be considered as evidence of free dipoles.

Measurement of Dielectric Constant

The dielectric constant ϵ of a substance is usually determined by measuring the capacitance of a condenser when it is filled with the material and when it is empty and using the relation,

$$\epsilon = \frac{C}{C_0}$$

where C and C_0 are capacitances with substance and vacuum respectively. If accurate values of ϵ are desired both C and C_0 must be corrected for edge effects.

If the substance under investigation forms large crystals readily or if it can be formed into a ceramic, a parallel plate condenser can be built and the absolute dielectric constant measured. Some materials, however, cannot be investigated in this way, but must be ground into a fine powder and packed into some form of suitably shaped condenser. The problem of obtaining ϵ_0 , the dielectric constant of the homogeneous crystal from ϵ , the measured dielectric constant of the powders has been undertaken by many authors⁸. Some have assumed that the molar polarizations defined by

$$[P] = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \quad (13)$$

⁸ Böttcher, C.J.F., Theory of Electric Polarisation, Elsevier, 1952.

where M is the molecular weight and d is the density, are additive. That is

$$[P] = \sum_k x_k [P_k] \quad (14)$$

where x_k is the mol. fraction of the k th component and $[P_k]$ is the mol. polarization of the k th component.

In the case of a mixture of crystalline powder and air the dielectric constant of air can be taken to be unity, and then this gives

$$\frac{\epsilon-1}{\epsilon+2} = \delta \cdot \frac{\epsilon_0-1}{\epsilon_0+2} \quad (15)$$

where $\delta = \frac{\text{volume of crystalline powder}}{\text{volume of condenser}}$

This formula gives values of ϵ_0 that are too large in some cases and in other cases gives negative values. The fault with this relation is that it is true only if the Lorentz formula for the local field is valid at all points in the powder. It also ignores possible effects due to the shape of the grains, causing a distortion of the field between them.

Weiner⁹ suggested using instead the relation

$$\frac{\epsilon-1}{\epsilon+u} = \delta \cdot \frac{\epsilon_0-1}{\epsilon_0+u} \quad (16)$$

He assumed u to be a function of particle size and shape and not a function of δ . Measurements on K.Cl powders have shown that u increases with increasing δ , but that it

⁹Weiner, O., Abh. math. phys. Kl. Sächs. Akad. Wiss. Leipzig, 32, 509, 1912.

depends very little on particle size.

This theory has been extended by Bruggeman¹⁰ who computed the dielectric constant of regularly arranged aggregates of particles of definite shape such as laminae, cylinders, and spheres. For spherical particles his calculations lead to

$$\frac{\epsilon_0 - \epsilon}{\epsilon_0 - 1} = (1 - \delta) \epsilon^{1/3} \quad (17)$$

For powders consisting of spherical particles, Böttcher¹¹ assumed the environment of a particle to be an infinite continuous dielectric with dielectric constant ϵ and assumed that the particle diameters are negligibly small compared to the diameter of the condenser. He obtained the result

$$\epsilon_0 = \frac{3\epsilon\delta + 2\epsilon(\epsilon - 1)}{3\epsilon\delta - (\epsilon - 1)} \quad (18)$$

It is difficult to check Bruggeman's and Böttcher's results because their assumption of an infinite dielectric necessitates the use of a very large condenser for the powder measurements. It has been shown using condensers of different sizes that a condenser of 500 cm³ volume is needed if grain size is of the order of 0.005 cm.

This practical limitation makes the powder measurement of absolute dielectric constant difficult, and the results uncertain.

¹⁰Bruggeman, D.A.G., Ann. Physik, (5), 24, 636, 1935.

¹¹Böttcher, C.J.F., Rec. trav. chim. 64, 47, 1945.

Measurement of Capacitance by the Bridge Substitution Method

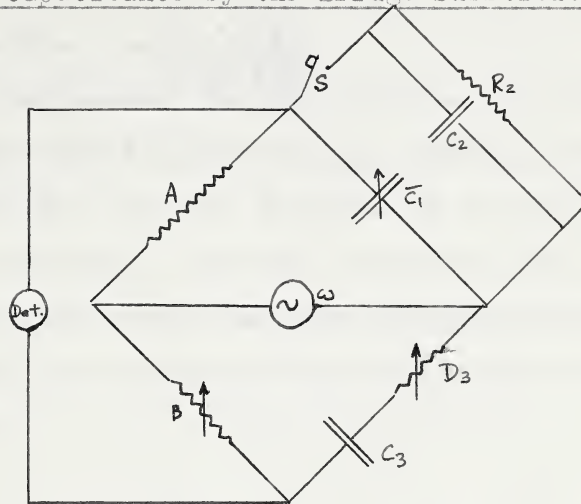


Fig 1: Bridge Used For Measuring Small Capacitances

Small capacitances, such as those encountered in the present work, can be conveniently and accurately measured by using an impedance bridge with a substitution method, in the circuit shown in Fig. I. To determine the value of the unknown capacitance C_2 the following procedure is followed.

(a) The switch S is opened and C_1 is set at some convenient value \bar{C}_1 .

(b) B is adjusted with D_3 set at zero until the detector shows no deflection.

(c) S is then closed, \bar{C}_1 is changed to C_1 and D_3 is varied until balance is obtained.

Applying the well known conditions for the balance of the bridge we arrive at the result:

$$C_2 = \bar{C}_1 - C_1 - \frac{\bar{C}_1 \omega^2 C_3^2 D_3^2}{1 + \omega^2 C_3^2 D_3^2} \quad (19)$$

If the leakage resistance, R_2 were infinite, the second term on the right would be zero and C_2 could be determined merely by subtracting the two settings, \bar{C}_1 and C_1 of the same variable condenser. However, in many of the measurements to be reported, there has been an appreciable apparent conductance, and the correction term in equation (19) has been necessary.

III APPARATUS AND PROCEDURE

Measurements on Powdered Samples

The apparatus and procedure were the same as those used by Young¹².

All powder measurements were made on samples that had been first powdered with a mortar and pestle and then passed through a sieve with a mean mesh spacing of 0.127 m.m. The sample was then placed in a dessicator over concentrated sulphuric acid for a period of twenty-four hours, after which it was transferred to the condenser cell.

The procedure of filling the cell consisted in placing small quantities of powder onto the filler cap with a knife blade then tapping the outside of the cell causing the powder to fall into the cell and assuring a reasonable amount of packing. Filling the cell and sealing it required about twenty minutes.

The condenser cell itself consisted of two concentric brass circular cylinders with the following dimensions:

Inner radius of outer cylinder 2.024 cm. \pm .0015

Outer radius of inner cylinder 1.895 cm. \pm .0015

Length of inner cylinder 8.628 cm. \pm .0015

Calculated capacitance neglecting edge effect 73.11 μ f.

¹² Loc. cit.

The brass cylinders were held rigidly in place by a threaded polystyrene holder at the bottom. A similar holder but lacking threads served as a top to the condenser. The entire cell was placed inside a brass can, the bottom of the cell being supported by three small polystyrene disks to decrease the thermal contact between the bottom of the cell and the outside can. Three brass spring contacts attached to the outer cylinder of the condenser provided thermal and electrical contact to the outer can. To guard against water vapor condensing on the condenser plates during the experiment, the top of the outer can was sealed completely about its edge with Wood's metal.

Temperature Control and Measurement

The temperature of the powder was varied by gradually lowering or raising the entire assembly in a Dewar flask at the bottom of which was between 50 to 100 cm³ of boiling liquid nitrogen or crushed solid carbon dioxide. The temperature change took place at a rate of about 20 - 30 degrees per hour. Because of the low thermal conductivity of the powder a temperature gradient of as much as three degrees existed between the cylinders of the cell. In all results, the temperature of the powder is taken as the mean of the outside and inside cylinder temperatures.

The temperatures of the cylinders were measured by

means of copper constantan thermocouples, the leads to which along with the electrical connection to the inner cylinder were passed through a one cm. diameter brass tube attached to the top of the outside can. Spring clips served to hold the thermocouples in place. Separate ice baths of finely crushed ice in glass funnels held the reference junction of each thermocouple. Each reference junction was a 1 cm. x 2 cm. brass plate. The thermal emfs were measured with a Leeds and Northrup type K1 potentiometer with a table galvanometer as null detector. Temperature measurements to within $\pm \frac{1}{2}$ degree centigrade were possible, and required about ten seconds to make.

The thermocouples were calibrated at the steam point by suspending the junctions at about two cm. depth in a beaker of boiling distilled water and at the boiling point of 99.6° pure liquid oxygen by a similar depth of suspension. The temperatures of calibration were obtained from the Handbook of Chemistry and Physics 35th edition, where the temperature of boiling water and of boiling liquid oxygen are given as functions of the air pressure. Values of thermal emf vs temperature for Cu - Constantan thermocouples were also obtained from the Handbook of Chemistry and Physics, 35th edition. The deviation of the thermocouple emfs from the values given in the Handbook were assumed to be proportional to the temperature in centigrade degrees, i.e. $\Delta E = bt$ where ΔE is the emf deviation, b is a constant for a given thermocouple and t is

the temperature. A curve of corrected emf vs. temperature was drawn using the value of b found from the thermocouple calibration.

Capacitance Measurements

The bridge substitution method described above was used to determine the cell capacitance, C_2 . The unknown capacitance C_2 was placed in parallel with a General Radio 722-D precision condenser, C_1 , which is variable from 0 to $1100 \mu\text{f}$ and can be read to $0.1 \mu\text{f}$. The capacitor C_2 could be put in the circuit or taken out by closing or opening the knife switch S . The remaining circuit elements were those of a General Radio impedance bridge. The condenser C_3 was a highly stable $.01 \mu\text{f}$ mica condenser. The resistor D_3 could be varied from 0 to 1600 ohms.

Signal voltage was supplied by a Hewlett Packard audio oscillator with the dial set at 5000 cycles and an output of about 22 volts. The detecting circuit consisted of a three stage amplifier, a band pass filter designed to pass only in the neighborhood of 5000 cycles and a Dumont oscilloscope with internal amplification of 200.

The bridge was first roughly balanced with C_1 set at about $1000 \mu\text{f}$ and S open by varying B and D_3 . For the remainder of the readings B was not changed. Full balance was then obtained by a slight adjustment of C_1 . The values of C_1 and

D, the dissipation factor were then recorded, D being small due to the small dissipation factor of the precision condenser. The switch S was then closed, C_1 and D were varied simultaneously until full balance was obtained, and the new values of C_1 and D were noted. Neglecting leakage, C_2 could be determined by subtracting the two settings of the precision condenser C_1 . Where leakage could not be neglected, in the higher temperature range, the difference in the two values of D was used in equation (19) to calculate the correction to C_2 .

Materials Used in Powder Measurements

The potassium alum was reagent grade $Al_2(SO_4)_3$.

$K_2SO_4 \cdot 24 H_2O$

Maximum limit of impurities:

Insoluble in H_2O	.005%
Cl	.0005
NH_3	.005
As	.001
Fe	.001
H.M.(as Pb)	.001
Na	.02

The aluminum sulphate used was supplied by British Drug Houses.

Measurements on Crystal Samples

The first attempts to grow crystals were made with

hydrated aluminum sulphate. Mellor¹³ states that aluminum sulphate crystals have been grown by using a supersaturated solution of aluminum sulphate in hydrochloric acid. Therefore, beakers of 50 cm³ volume were filled with solutions of from 0.1 normal to 12 normal hydrochloric acid and aluminum sulphate and the solutions were covered and allowed to evaporate slowly. No single crystal growth was observed but a crystalline crust formed on the 0.1 normal solution could have been formed into plates of suitable size for use in a parallel plate condenser.

Large potassium alum crystals were prepared by first obtaining seed crystals from 50 cm³ beakers filled with supersaturated solution and then placing the best formed octahedral seed crystals in a covered porcelain tray containing a depth of about 5 cm. of supersaturated solution. Every two days the crystals were turned over and the solution filtered to remove additional seed crystals that had formed.

After about two months' duration, flat octahedral crystals of about 4 to 6 cm² in area and one cm. in thickness were obtained. These crystals were then sawed into halves and each half was ground on fine emery paper to a thickness of about 1 m.m. To insure uniform thickness in the finished crystal plates, the crystal halves were glued with celluloid

¹³ Mellor, J.W., A Comprehensive Treatise of Theoretical and Inorganic Chemistry.

lacquer to a flat glass plate around whose edge a one cm. width of 1 mm. thick glass plate was glued. By grinding the exposed crystal on a flat emery surface it was possible to obtain thicknesses differing at most by 5% from the mean thickness.

Rectangular pieces were cut from the finished plates and mounted with celluloid lacquer to the upper plate of the condenser cell. The finished plate was placed in a dessicator for 24 hours and then the lower condenser plate was glued and pressed firmly into place. A coating of celluloid lacquer was then applied to the outside edge of the finished condenser, completely sealing it from the outside air.

The dimensions of the assembled parallel plate condenser were:

Average thickness of upper plate	$.077 \pm .001$ cm.
Average thickness of lower plate	$.025 \pm .001$ cm.
Average diameter	$7.227 \pm .003$ cm.
Average dielectric thickness	$0.130 \pm .004$ cm.
Calculated capacitance	$27.9 \mu\text{mf}$

Both plates were of polished brass. Pressure clips attached to the top of the upper plate and the bottom of the lower plate served to hold the thermocouple junctions.

The condenser was suspended inside an iron can which served as a constant temperature chamber. Suspension was provided by means of four brass prongs which were soldered so

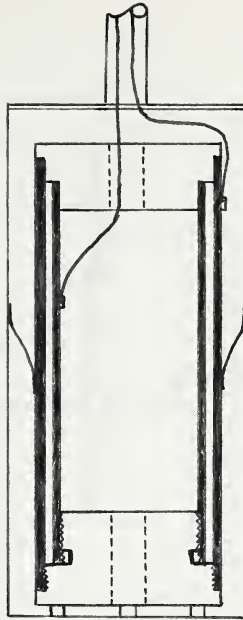
that they stood vertically on the bottom of the can. The prongs were pointed so that they fitted easily into brass sockets soldered to the bottom plate. This method of suspension provided rigidity as well as good electrical and thermal contact between the bottom plate and the bottom of the outside can.

The entire assembly was suspended inside a 12 cm. diameter porcelain basin at the bottom of which was a 5 cm. depth of solid carbon dioxide. The temperature of the condenser was varied by gradually raising or lowering the assembly in the same manner as was done in the powder measurements.

The temperatures of the upper and lower condenser plates were measured with copper-constantan thermocouples that had been calibrated at the steam point and at the sublimation point of carbon dioxide. A deviation curve for each thermocouple was drawn using data from the Handbook of Chemistry and Physics 35th edition.

The capacitance of the condenser was measured with exactly the same method as was used for the powder measurements.

(a)



(b)

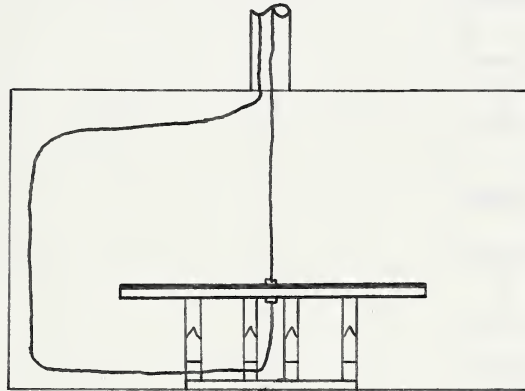


Fig 2: (a) Cylindrical Condenser and Outside Can
(b) Parallel Plate Condenser and Outside Can

Scale - 3:2

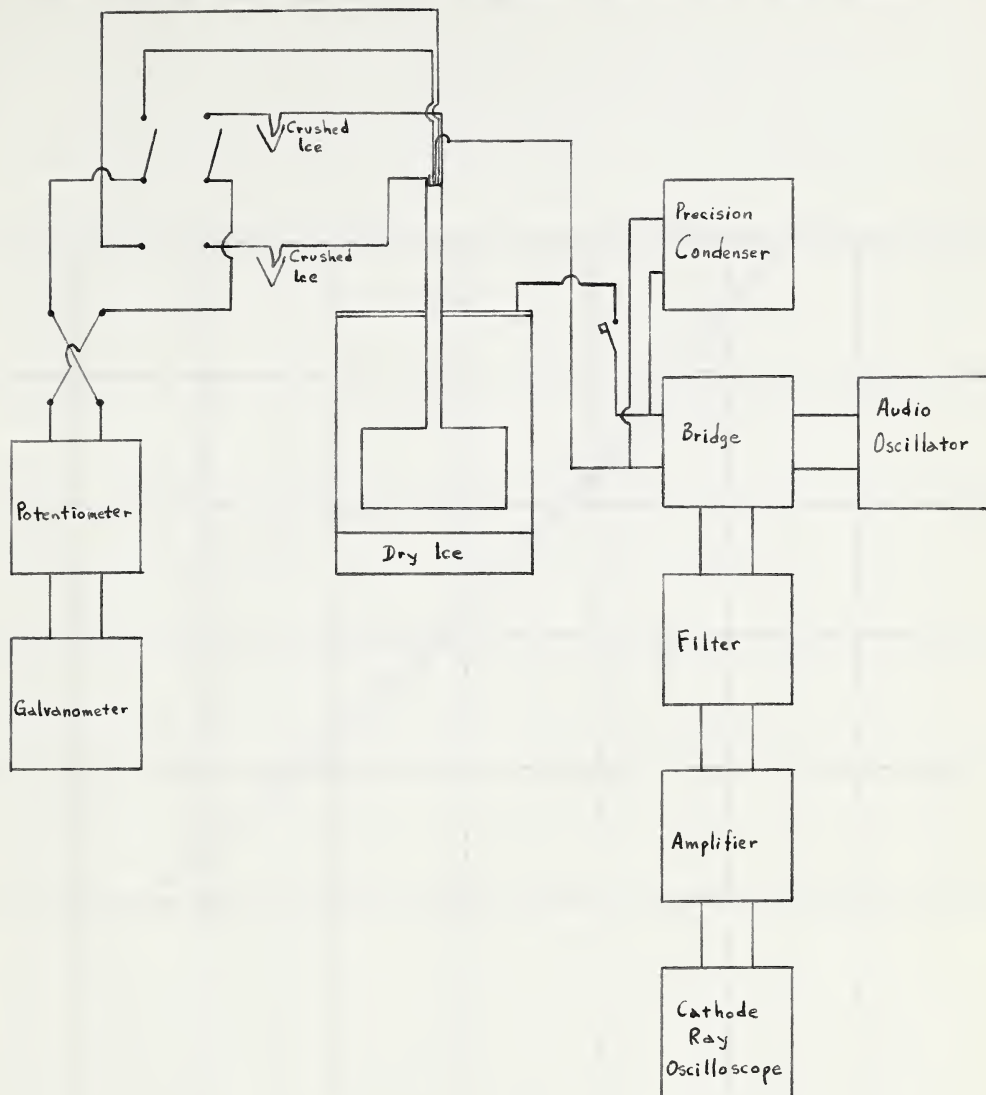


Fig. 3-Block Diagram of Assembled Apparatus

Fig 4- Dielectric Constant ϵ_0 and Dissipation Factor D vs. Temperature T
For $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Crystals Cut in the $\{111\}$ Planes

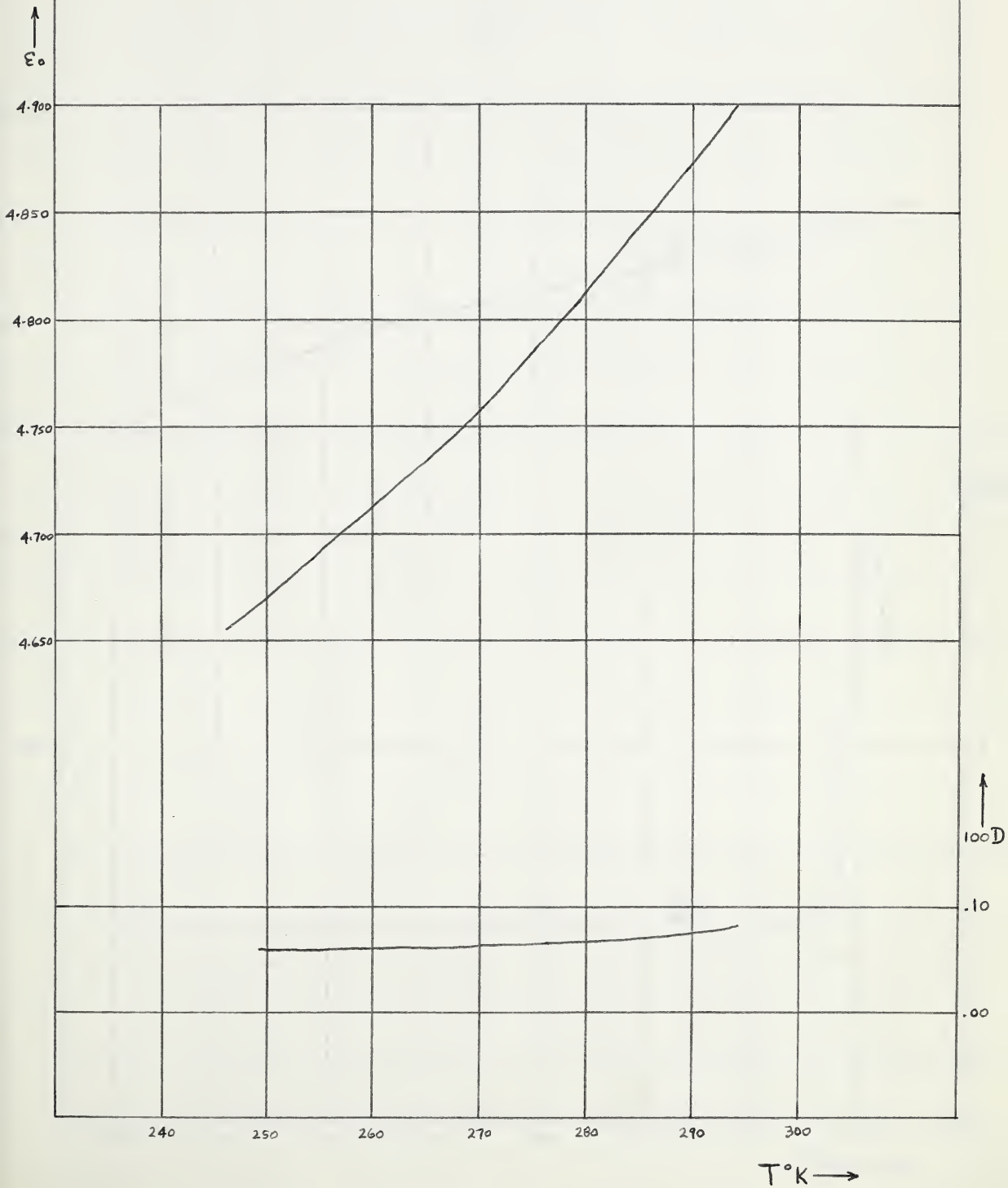


Fig 5- Dielectric Constant ϵ and Dissipation Factor D vs. Temperature T
For Powdered $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 17H_2O$

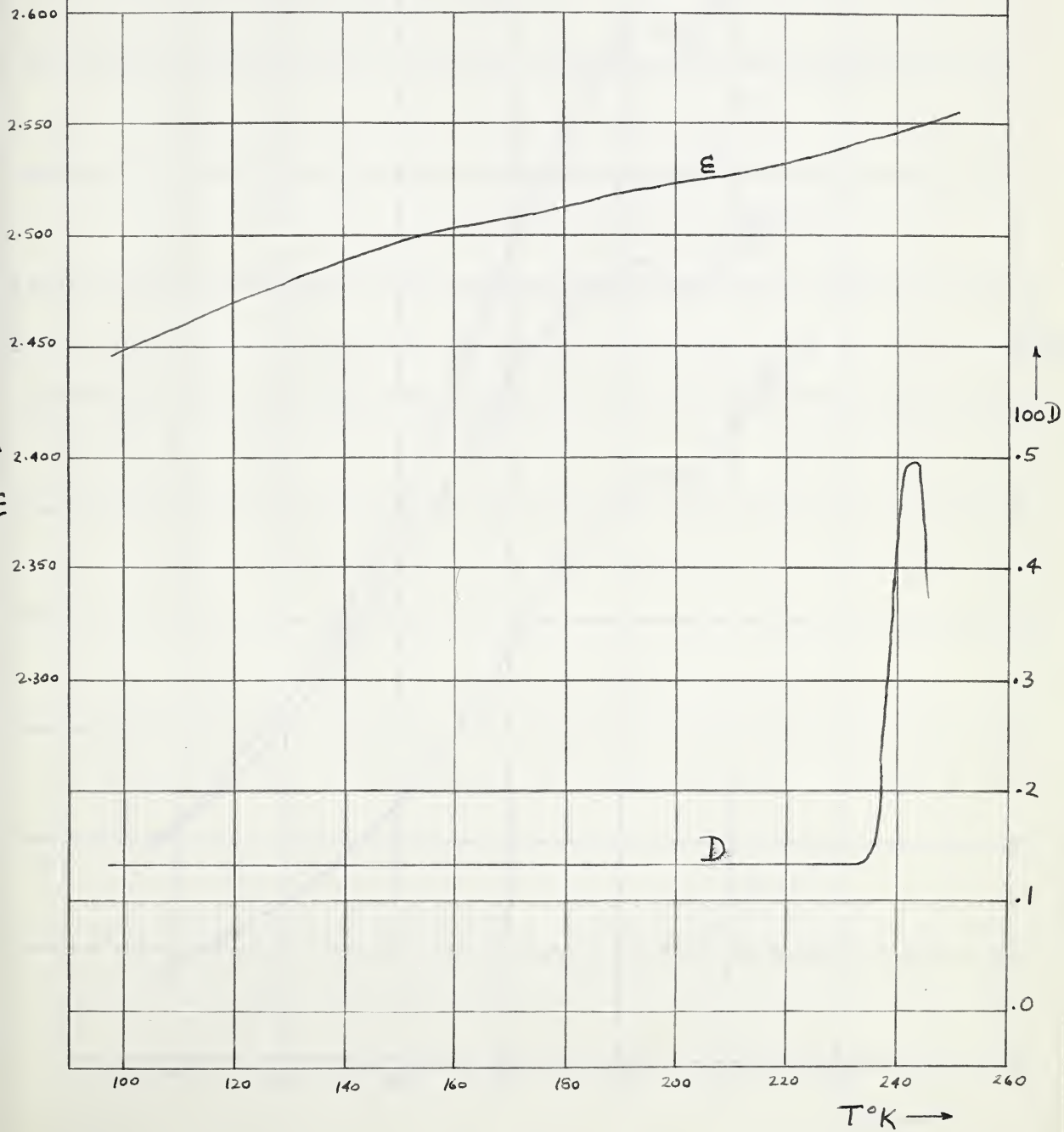


Fig 6 - Dielectric Constant ϵ and Dissipation Factor D vs. Temperature T
 Also, Corrected Dielectric Constant $\bar{\epsilon}$, Assuming D Due to Leakage, vs. T
 For Powdered $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

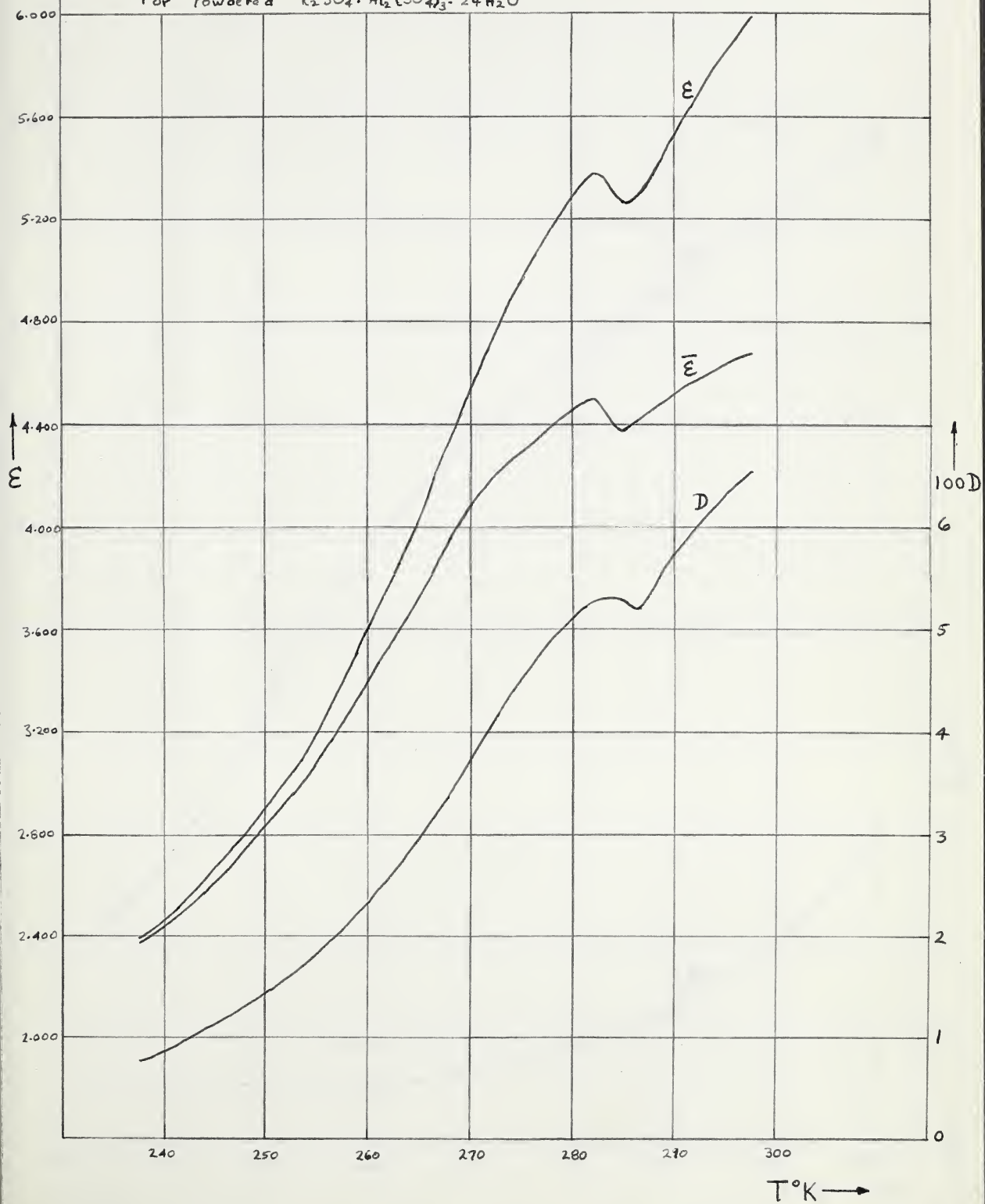


Fig 7 - Dielectric Constant ϵ and Dissipation Factor D vs. Temperature T
For Powdered $\text{Al}_2(\text{SO}_4)_3 \cdot 15 \text{H}_2\text{O}$

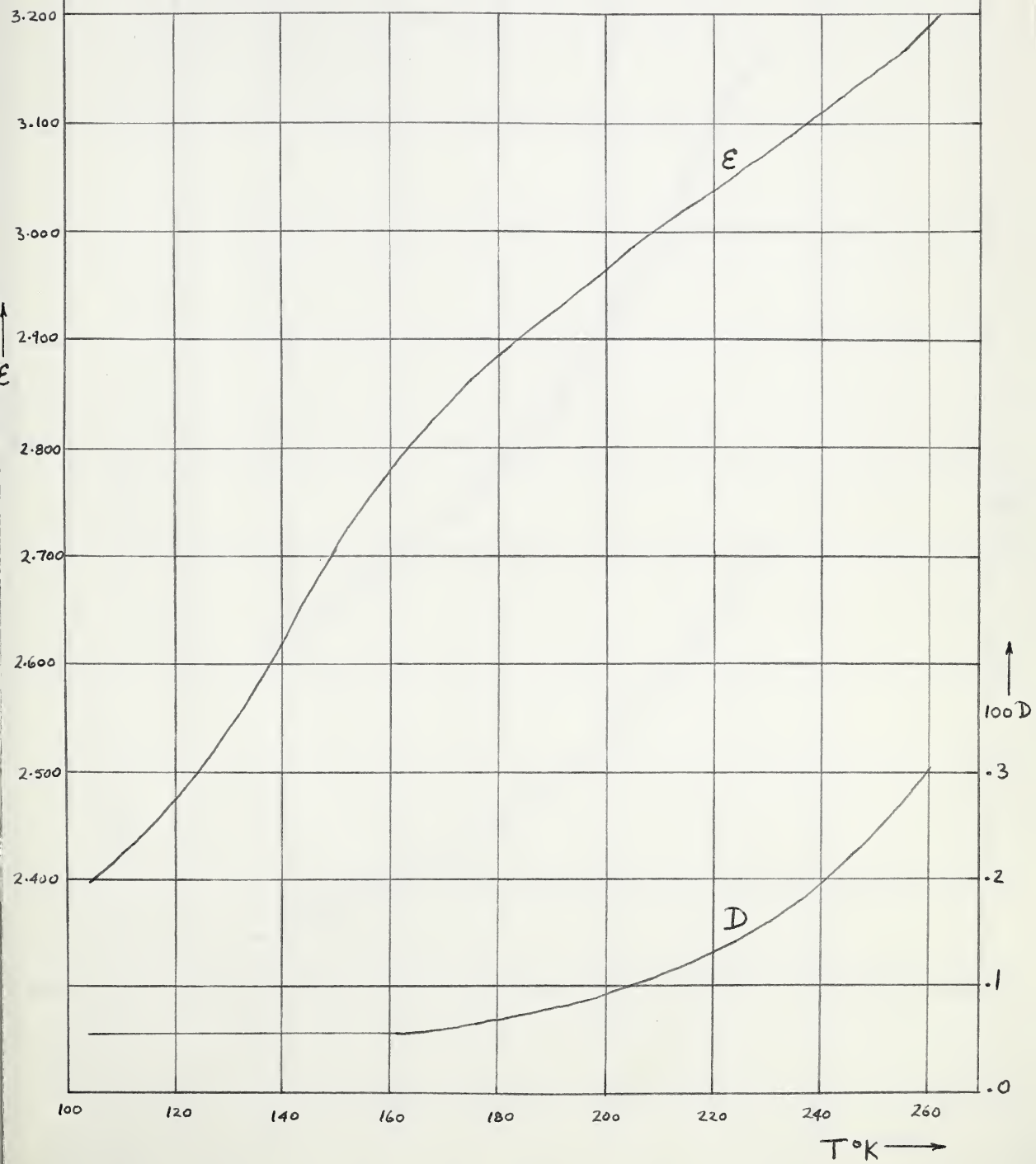


Fig 8 - Dielectric Constant ϵ and Dissipation Factor D vs. Temperature T
For Powdered $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$

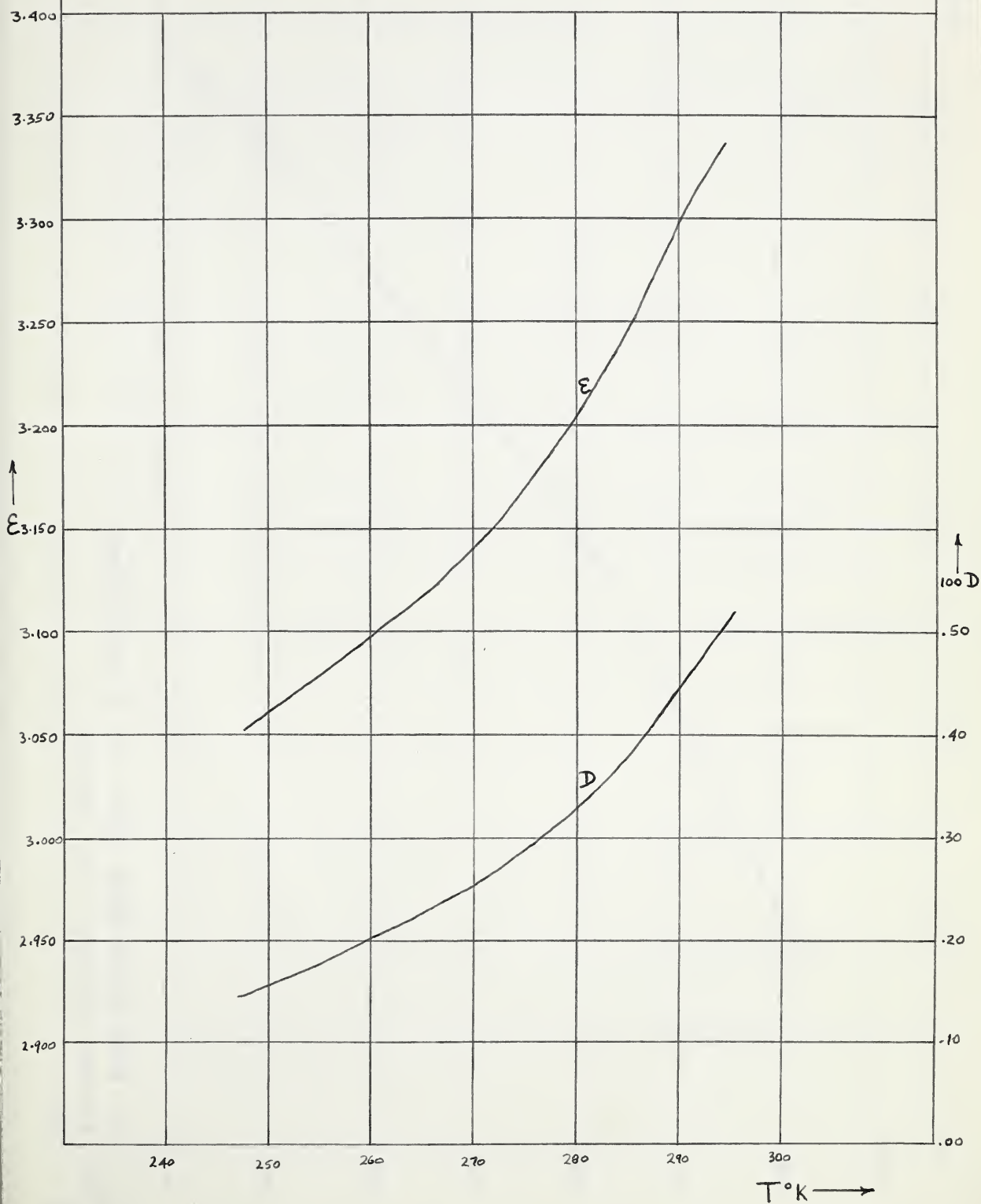
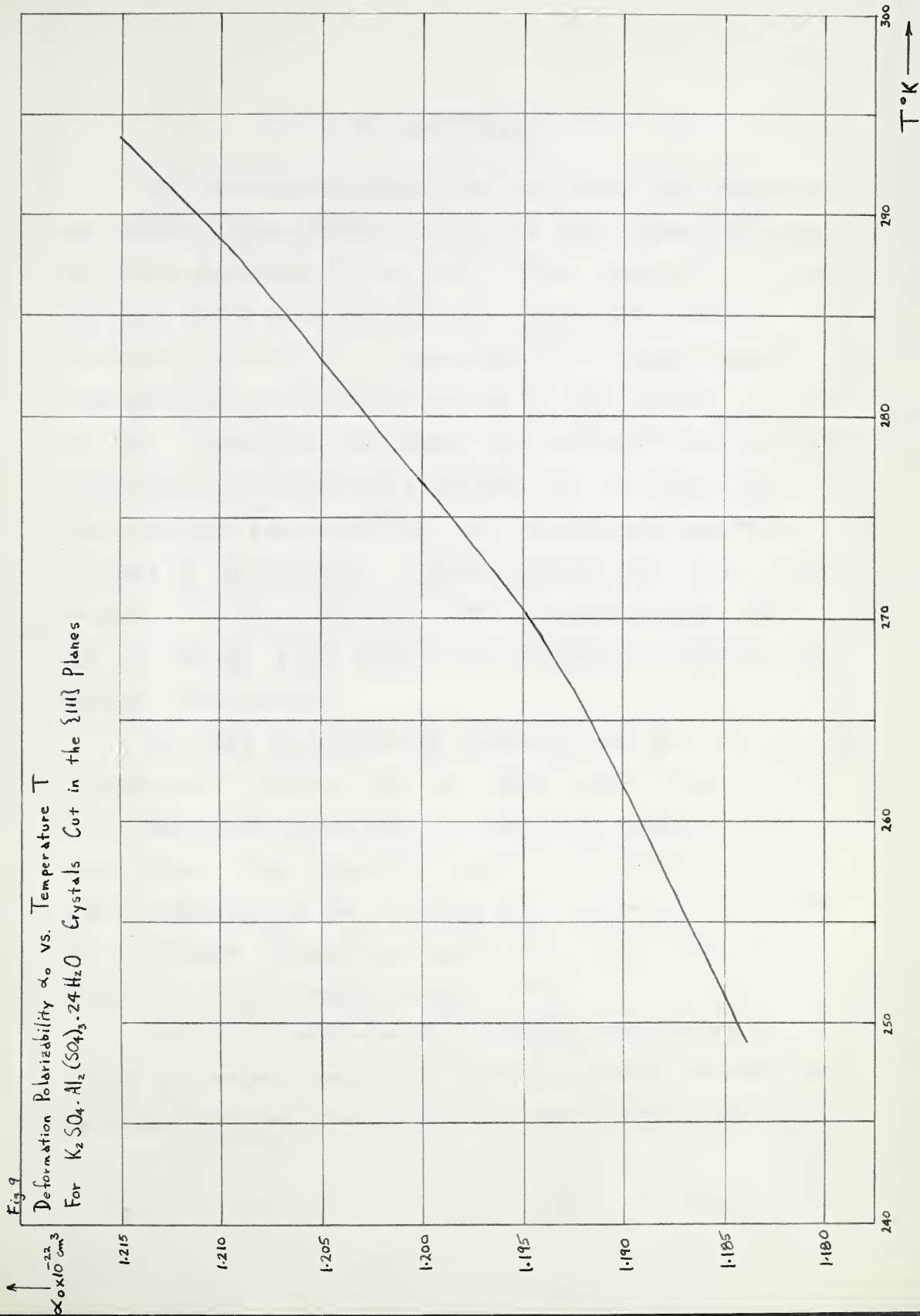


Fig. 9
Deformation Polarizability α_0 vs. Temperature T
For $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Crystals Cut in the $\{111\}$ Planes



IV DISCUSSION

The dielectric constant, ϵ_0 , and dissipation factor, $\tan \delta$, for potassium alum crystals cut in the (111) planes have been plotted as functions of the average plate temperature, T , over the range 250°K to 300°K. (Fig. 4). Since ϵ_0 is a slowly increasing function of T , the possibility of orientational polarizability is eliminated, as can be seen from eq. (9) or eq. (11). Therefore, only ionic and electronic polarizability contribute to the dielectric constant and the deformation polarizability can be computed as a function of temperature by means of the Clausius - Mosotti equation, eq. (8), N being obtained from the molecular weight of potassium alum, 948.8, and its density, 1.75, given by the Handbook of Chemistry and Physics, 35th edition.

The plot of deformation polarizability as a function of temperature is shown in Fig. 9. Theoretically, there should be no temperature dependence of deformation polarizability since elastic displacement of charge is responsible, but the ionic polarizability may increase with increasing temperature due to lattice expansion giving the ions more freedom to be displaced by the external electric field.

Values of the dielectric constant and dissipation factor for powdered samples of hydrated aluminum sulphate and potassium alum over the temperature range 100°K to 300° are

shown in Figs. 5, 6, and 8 plotted as functions of the average measured temperature of the inner and outer cylinders.

In Fig. 6, the corrected values of the dielectric constant for the potassium alum powder, are also shown plotted against temperature assuming that the dissipation factor is due entirely to conductivity across the cell.

A factor which affects the measured dielectric constant is the electrical conductivity of the dielectric, an increasing conductivity producing an increase in the measured dielectric constant. If we assume that the dissipation factor of the parallel condenser arrangement is due largely to electrical conduction across the experimental cell, the correction which must be subtracted from the measured capacitance can be computed using relation (19). The resulting corrected values of dielectric constant compare more favorably with the values obtained from the parallel plate condenser than the uncorrected values do.

The dissipation factor, D , of the parallel arrangement reaches its highest observed values in the measurements on potassium alum Fig. 6 its highest value being about .065 at 297°K. In the other tests D does not exceed 0.005.

Relatively high values for D were also observed by Young¹⁴ in his measurements on: $\text{Cr}_2 (\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, where D

¹⁴Loc. cit.

reached 0.060 at 243°K; $\text{Cr}_2 (\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ with a value of 0.090 at 252°K; $\text{Cr}_2 (\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ with a value of 0.037 at 257°K and on $\text{Cr}_2 (\text{SO}_4)_3 \cdot 15 \text{H}_2\text{O}$, D reached 0.060 at 264°K.

In all tests in which D rises steeply in the range 240°K to 260°K, the measured value of the dielectric constant also rises rapidly. According to Young, $\text{Cr}_2 (\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ at 250°K had a rate of change of dielectric constant of 0.975 in six degrees of temperature change while D changes from 0.083 to 0.090. At 150°K, however, the dielectric constant changes by only 0.013 and D by 0.00 in a six degree temperature change.

The occurrence of the rapid rise of D along with the rapid rise in dielectric constant observed in the powder measurements on hydrated chromium sulphate and potassium alum over the temperature range 240°K - 300°K is consistent with an increase with temperature of the electrical conductivity of the powder specimens.

Measurements on powdered potassium alum indicate the existence of a dielectric anomaly with a sharp peak in dielectric constant occurring at 282°K. This anomaly, however, is not a real anomaly because no indication of its presence was revealed in the measurements on the alum crystals.

The cause of the large increase in dissipation factor observed for the powders in the range 240° to 300°K is almost certainly a surface phenomenon, since it is not observed in

measurements on the crystal plates. Two surface phenomenon possible are ionic conductivity and dielectric absorption. Either of these could occur if there were a layer of adsorbed water on the powder grains. Measurements with a Meggar of the conductivity of potassium alum powder showed an increase of conductivity with temperature beginning at about 240°K , below which the conductivity was zero. The conductivity, however, was very small so the amount of water must have been small. The adsorbed water probably affects the results by forming charged layers on the surface of the particles. This may require an appreciable time to come to equilibrium and so causes dielectric absorption and an apparent conduction.

The final conclusion is that the rapid rise in dielectric constant and dissipation factor in the temperature range 240°K to 300°K observed by Sturrock, Young, and the author is due to adsorbed water, even when the powder was carefully dessicated and when analysis showed amounts of water present less than the equilibrium water of crystallization.

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